

**TITLE****ONE-PACK PRIMER SURFACER COMPOSITION FOR SMC  
AUTOMOTIVE BODY PANELS**

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**BACKGROUND OF THE INVENTION**

The present invention relates to a coating composition useful as a primer surfacer over SMC (sheet molding compound) and other molded thermoset plastic parts, and more particularly to a primer surfacer composition for use over previously sealed SMC automotive body panels, which composition has the ability to seal post-sealer stress defects in the SMC body panel before the exterior topcoat finish is applied to the vehicle.

Sheet molding compound (SMC) has gained widespread use in the automotive industry as a molding compound for exterior vehicle parts, due to its ability to deliver all of the structural properties of metal, while introducing other advantages such as lower vehicle body weight, lower tooling costs, an increase in vehicle part styling freedom, and its inherent corrosion resistance. Nowadays, SMC is widely used for high-volume moldings of large, rigid, exterior automotive body panels such as hoods, fenders, and grills. In such applications, SMC can deliver the advantages of plastic while concealing from an observer that the panel is a form of plastic because of its rigid strength and its steel-like surface quality. SMC can also be processed easily through assembly lines that handle steel because it can run through the traditional electrodeposition process and withstand the topcoat bake temperatures encountered in the Original Equipment Manufacturer (OEM) process.

One difficulty with SMC as well as other molded fiber reinforced thermoset plastics is its surface porosity. When parts made from these plastics are coated, defects called pops occur in the paint. These defects are caused by evolution of gases trapped in the porous substrate during the oven cure cycles of the subsequently applied coating layers. These defects usually show up after application of the automotive primer surfacer and can cause extensive reworking and repainting of the part. Attempts have been made to eliminate the problem by applying SMC sealers to the part at the molding plant before the part is shipped and attached to the unpainted vehicle frame at the auto assembly plant. However, most liquid SMC sealers in use nowadays, for example, one-pack melamine and two-pack isocyanate systems, are very brittle and while they may reduce some porosity popping, they are easily damaged and cracked during shipping and



handling operations at the OEM assembly plant, and popping defects are still observed. Recent attempts have been made to utilize sealers based on silane-carbamate-melamine curing systems in order to reduce popping by increasing flexibility which reduces post-sealer stress damage, as for example, as taught in  
5 copending U.S. Patent Application No. 10/623,710. Yet some topcoat popping still occurs. It would be helpful if the first coating layer applied to the SMC part at the OEM assembly plant, i.e., the primer surfacer, had sealing capability, to seal the stress-induced defects that occurred after the SMC sealer was applied, so that pop defects visible in the topcoat layer could be eliminated. Existing primer  
10 surfacers, however, are generally not effective sealers.

Therefore, a need exists for a primer surfacer composition suited for use over the entire vehicle body, including both the electrocoat primed metal frame and molded SMC and other parts attached thereto, that exhibits excellent sealing ability over damaged SMC parts which minimizes extensive reworking and  
15 repainting of the part, while also meeting today's performance requirements, such as excellent chip and crack resistance, outstanding corrosion resistance, and excellent adhesion to sealed SMC body parts and providing a smooth and even surface to which the exterior automotive topcoat finishes will adhere.

The novel coating composition of this invention has the aforementioned  
20 desirable characteristics.

### **SUMMARY OF THE INVENTION**

The present invention is directed to a one-pack type coating composition useful as a primer surfacer sealer composition in the manufacture of automobiles  
25 and trucks, containing a film forming binder and an organic liquid carrier, wherein the binder comprises:

(a) from about 10-90% by weight, based on the weight of the binder, of a low molecular weight silane functional compound with a hydrolyzable group and preferably at least one additional functional group (urea, urethane and/or  
30 hydroxyl) that is capable of reacting with crosslinking component (d);

(b) from about 0-70% by weight, based on the weight of binder, of low molecular weight polyol compound, oligomer or polymer;

(c) from about 0-15% by weight, based on the weight of the binder, of a silane coupling agent;



(d) from about 10-90% by weight, based on the weight of binder, of melamine formaldehyde crosslinking agent; and

(e) from about 0-40% by weight, based on the weight of binder, of an additional crosslinking agent selected from a blocked polyisocyanate.

5            Optionally, the composition further includes one or more dispersed particles with at least one functional group (urea, urethane, silane or hydroxyl) capable of reacting with (a) or (d), preferably 0 to 10% by weight, based on the weight of binder, to minimize cracking. The composition also typically contains pigments in a pigment to binder ratio of about 1:100-150:100, particularly when  
10        used as a primer surfacer.

             The coating composition of this invention forms a high quality coating having the aforementioned desirable characteristics, and provides a surface to which conventional topcoats will adhere, and is particularly useful as a primer surfacer composition to cover imperfections in surfaces of both electrocoat primed  
15        metal parts and molded plastic parts such as SMC that are used in the manufacture of automobiles and trucks.

             The claimed invention further includes a method for reducing the incidence of popping defects appearing on molded SMC and other plastic parts, particularly auto parts, which comprises applying to previously painted (i.e.,  
20        previously sealed) molded SMC part or other plastic part, a coating layer of the forgoing composition and curing the coating layer thereon. Molded SMC and other plastic parts coated/sealed with the forgoing composition also form part of this invention.

             As used herein:

25            "One-pack" coating composition means a thermoset coating composition containing reactive components that are stored in the same container but are unreactive during storage.

             "SMC" means a sheet molding compound. It is the plastic material most commonly used in the compression molding of plastic automotive body panels and other rigid automotive parts. SMC is a compound composed generally of  
30        polyester resin, fillers, catalysts, chopped glass fibers, release agents and a low profile additive that expands during the curing reaction. SMC has been described in various patents including U.S. Pat. Nos. 3,577,478, 3,548,030 and 3,466,259.

             A "pop defect" is a sharp-edged circle in the cured coating often about 1  
35        mm in size caused by gases escaping from or through the film during curing.



Typically a pop develops during baking when paint forms a skin before all vapors are expelled. Trapped gases rupture the surface skin as they exit the film, forming the defect. Visually a pop appears as a volcano in appearance, however if it occurs early enough for some reflow to occur it may appear as a pinhole or dimple and if  
5 the surface of the coating has attained sufficient strength the gases may not be able to penetrate the film and in this case will form a bubble or bulge on the coating surface.

### **BRIEF DESCRIPTION OF THE DRAWING**

10 FIG. 1 is a graphical illustration showing a significant reduction in the amount of post-stress pop defects appearing in the topcoat finish when a sealed SMC part is coated with the primer surfacer composition of the present invention, when compared to SMC parts coated with commercial primer surfacers.

### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

To reduce or eliminate paint pop defects caused by damage to the SMC sealer during shipping and handling operations at vehicle assembly plants, it is desired to have a primer surfacer coating over sealed SMC parts that not only has the ability to provide a smooth and even surface to which the exterior top coat  
20 finishes will adhere, but that also has the ability to seal and not have paint pops appear on the surface of molded SMC parts and/or other thermoset or thermoplastic plastic parts, reinforced and not reinforced, used in the manufacture of automobiles and trucks. The primer surfacer composition of this invention (also referred to herein as a "primer surfacer sealer composition") provides such  
25 sealing capabilities, while also meeting today's performance requirements, such as low VOC (volatile organic content) emission requirements, excellent chip and crack resistance, outstanding corrosion resistance, good sandability, and excellent adhesion to e-coated steel and to sealed SMC body parts and provides a smooth and even surface to which the exterior automotive topcoat finishes will adhere. In  
30 addition to these properties, if desired, the primer surfacer of this invention can be rendered sufficiently conductive to further facilitate subsequent electrostatic spraying of automotive exterior topcoat finishes thereon. The present inventors have discovered a coating composition that offers the forgoing properties, without sacrificing processability and sprayability.

35 Preferably, the coating composition of the present invention is formulated as a high solids composition. By "high solids composition", it is meant having a



relatively high binder solids content in the range of from 40 to 100 percent by weight, based on the total weight of the composition. The coating of the present invention is also preferably a low VOC (volatile organic content) coating composition which meets today's pollution requirements, which means a coating  
5 that includes less than 0.6 kilograms of organic solvent per liter (5 pounds per gallon) of the composition, preferably in a range between 0.18 and 0.48 kilograms of organic solvent per liter (1 to 4 pounds per gallon) of the composition, as determined in accordance the procedure provided in ASTM D3960.

The film-forming portion of the present composition is referred to as the  
10 "binder" or "binder solids" and is dissolved, emulsified or otherwise dispersed in an organic solvent or liquid carrier. The binder generally includes all the normally solid compounds or polymeric non-liquid components of the composition. Generally, catalysts, pigments, or chemical additives such as stabilizers are not considered part of the binder solids. Non-binder solids other  
15 than pigments usually do not amount to more than about 5-10% by weight of the composition. In this disclosure, the term binder includes the silane functional compound, the melamine crosslinking agent, and all other optional compounds and/or oligomeric and/or polymeric film-forming ingredients.

The coating composition of the present invention includes both silane and  
20 melamine components in the binder. The silane component used in the composition is a silane functional compound with at least one hydrolyzable group (alkoxy group) on the silane group and at least one additional functional group (urea, urethane and/or hydroxyl) that is capable of reacting with the melamine crosslinking component. Among the hydrolyzable groups alkoxy groups such as  
25 methoxy group and ethoxy group are preferable because of the mild hydrolyzability thereof. The coating composition includes in the range of from 10 to 90%, preferably in the range of from 10 to 40%, and most preferably in the range of from 10 to 35% of the silane component, the percentages being in weight percentages based on the total weight of binder solids.

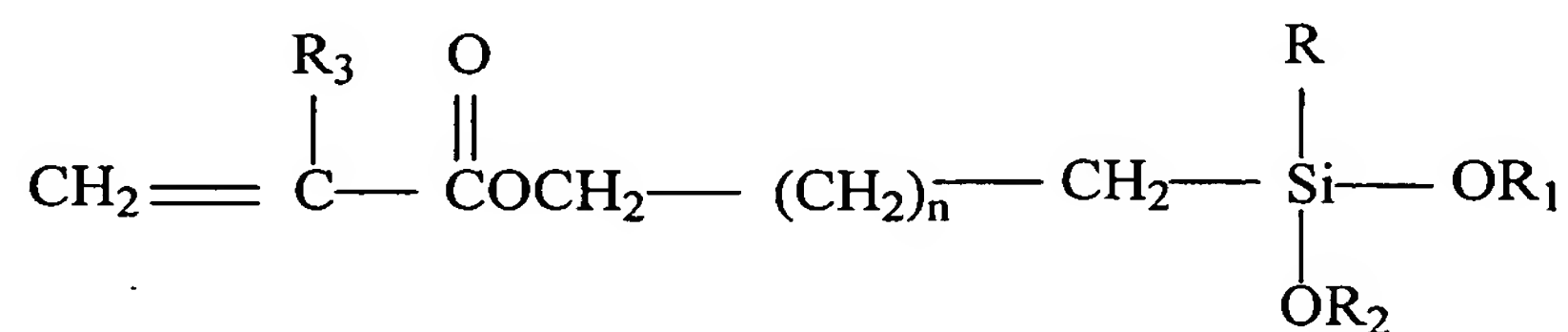
30 It is generally preferable that the silane component used herein have a relatively low weight average molecular weight not exceeding 5,500, more preferably in the range of about 179 to 4,500 and most preferably in the range of about 250 to 3,500. All molecular weights disclosed herein are determined by gel permeation chromatography (GPC) using a polystyrene standard.

35 Such silane functional components may be prepared by a variety of techniques. For example, the compound may be conventionally polymerized from ethylenically unsaturated silane containing monomers, along with suitable



ethylenically unsaturated hydroxy containing monomers and/or urethane/isocyanate functional monomers to produce either a hydroxy containing silane oligomer, a urethane containing silane oligomer, and/or an isocyanate containing silane oligomer. The isocyanate functional groups if any may then be further reacted with a hydroxy functional material to make a urethane containing silane oligomer. The reaction conditions should be chosen so that 100% of the isocyanate groups are reacted, or as close to 100% as can be reasonably achieved, so that essentially no free isocyanate groups (which are highly reactive with the other binder components) remain, since it is desired to store together all binder components in the same container and provide a one-pack composition.

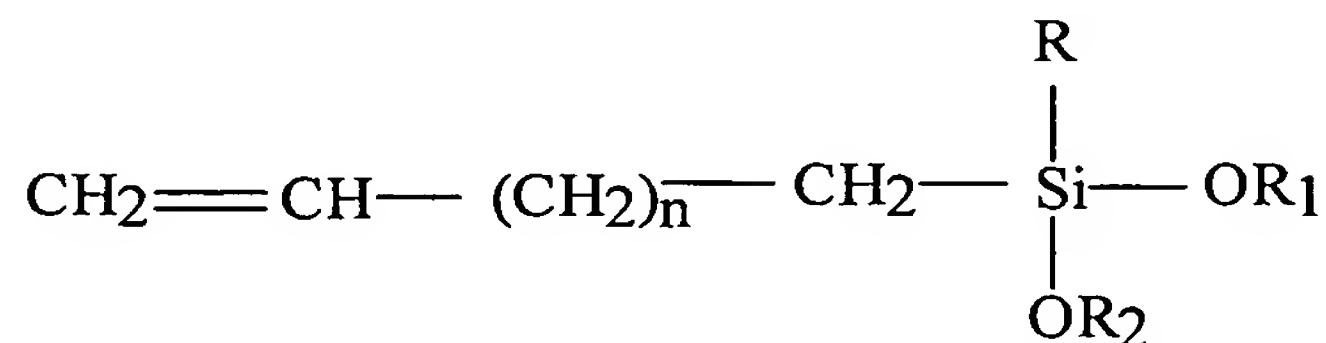
A suitable silane containing monomer useful in forming the silane oligomer cited above is an alkoxysilane having the following structural formula:



wherein R is either CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, CH<sub>3</sub>O, or CH<sub>3</sub>CH<sub>2</sub>O, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O; R<sub>1</sub> and R<sub>2</sub> are CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, or CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>; and R<sub>3</sub> is either H, CH<sub>3</sub>, or CH<sub>3</sub>CH<sub>2</sub>; and n is 0 or a positive integer from 1 to 10, preferably from 1 to 4. Preferably, R is CH<sub>3</sub>O or CH<sub>3</sub>CH<sub>2</sub>O and n is 3.

Typical examples of such alkoxysilanes are the acrylatoalkoxy silanes, such as gamma-acryloxypropyltrimethoxy silane and the methacrylatoalkoxy silanes, such as gamma-methacryloxypropyltrimethoxy silane, and gamma-methacryloxypropyltris(2-methoxyethoxy) silane.

Other suitable alkoxy silane monomers have the following structural formula:



wherein R, R<sub>1</sub> and R<sub>2</sub> are as described above and n is a positive integer from 1 to 10, preferably from 1 to 4. Examples of such alkoxysilanes are the vinylalkoxy



silanes, such as vinyltrimethoxy silane, vinyltriethoxy silane and vinyltris(2-methoxyethoxy) silane.

Other suitable silane containing monomers are acyloxysilanes, including acrylatoxy silane, methacrylatoxy silane and vinylacetoxysilanes, such as vinylmethyldiacetoxysilane, acrylatopropyltriacetoxysilane, and methacrylatopropyltriacetoxysilane. It is understood that combinations of the above-mentioned silane containing monomers are also suitable.

Suitable hydroxy containing monomers which can be used to place reactive hydroxy groups on the silane compound include hydroxy alkyl acrylates or methacrylates having 1-8 carbon atoms in the alkyl group, for example, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate and the like. Suitable isocyanate containing monomers which may be used to place isocyanate/urethane functional groups on the silane compound include 2-isocyanato-ethyl methacrylate,  $\alpha$ ,  $\alpha$ -dimethyl, meta-isopropenyl benzyl isocyanate and the like.

Other non-silane containing monomers can also be used for the purpose of achieving the desired properties such as hardness/flexibility and adhesion. Suitable ethylenically unsaturated non-silane containing monomers are alkyl acrylates, alkyl methacrylates and any mixtures thereof, where the alkyl groups have 1 to 12 carbon atoms, preferably 3 to 8 carbon atoms.

Suitable alkyl methacrylate monomers that can be used include methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, pentyl methacrylate, hexyl methacrylate, octyl methacrylate, nonyl methacrylate, and lauryl methacrylate. Similarly, suitable alkyl acrylate monomers include methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, pentyl acrylate, hexyl acrylate, octyl acrylate, nonyl acrylate, and lauryl acrylate. Cycloaliphatic methacrylates and acrylates also can be used, for example, such as trimethylcyclohexyl methacrylate, trimethylcyclohexyl acrylate, isobornyl methacrylate, isobornyl acrylate, t-butyl cyclohexyl acrylate, or t-butyl cyclohexyl methacrylate. Aryl acrylate and aryl methacrylates, such as, for example, benzyl acrylate and benzyl methacrylate can be also used. It is understood that combinations of the foregoing monomers are also suitable.

In addition to alkyl acrylates or methacrylates, other polymerizable non-silane-containing monomers, up to about 50% by weight of the compound, can be



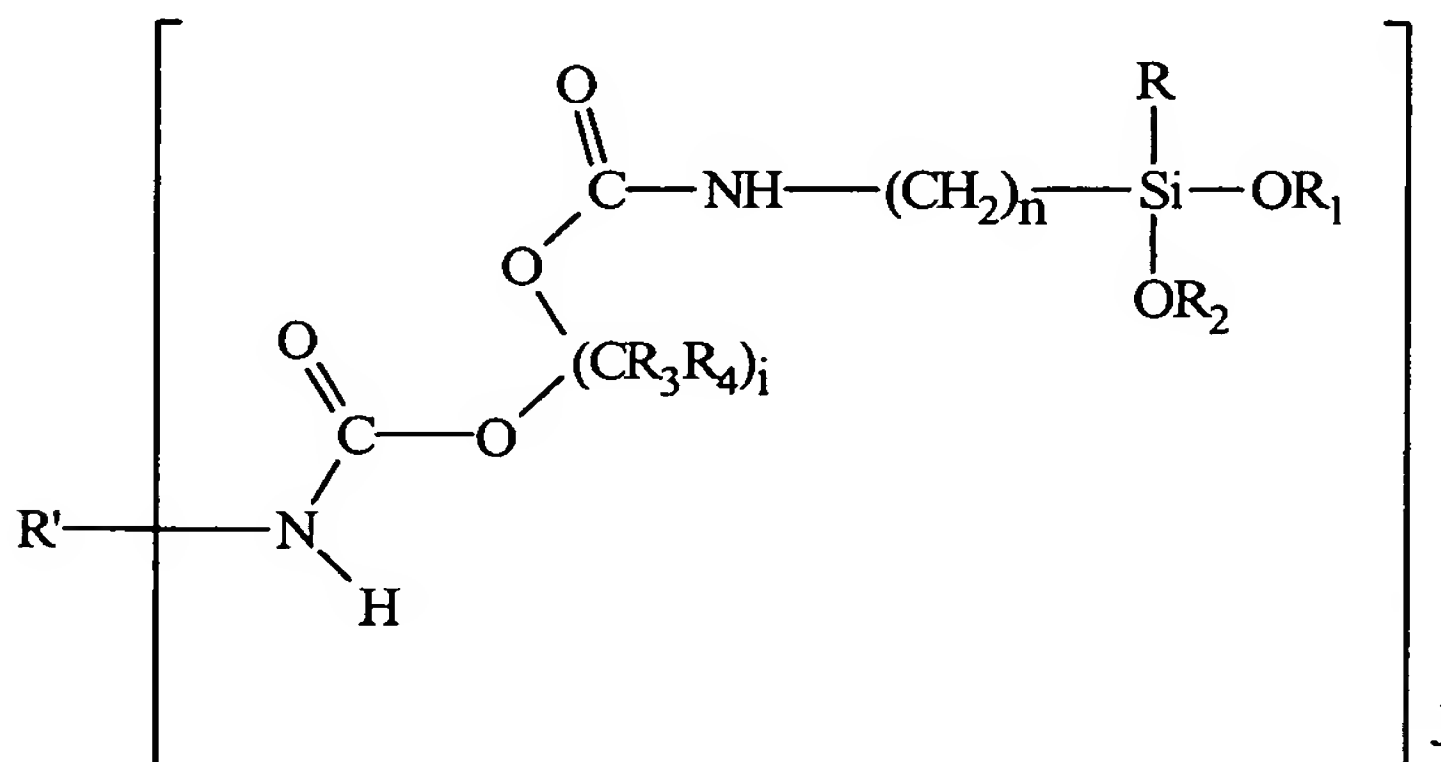
used in the silane compound for the purpose of achieving the desired properties. Exemplary of such other monomers are styrene, methyl styrene, acrylamide, acrylonitrile and methacrylonitrile.

Another type of silane compound that can be used in the present invention is, for example, the reaction product of a silane containing compound, having a reactive group such as epoxide or isocyanate, for example, 3-glycidylpropyl trimethoxysilane or isocyanatopropyl triethoxysilane, with a non-silane containing compound having a reactive group, typically a hydroxyl or an epoxide group, that is co-reactive with the silane. An example of a useful compound is the reaction product of a polyol and an isocyanatoalkyl alkoxysilane such as isocyanatopropyl triethoxysilane.

Urea containing silane compounds can also be used in the present invention. Urea functionality can be readily obtained by one skilled in the art by reacting an isocyanate containing silane compound with an amine or polyamine or  
15 by reacting an amine containing silane compound with an isocyanate or polyisocyanate.

Still another suitable silane compound that can be used in the present invention is to react an amine containing silane compound with a substance reactive with said amine functionality. The preferred method for preparing such a silane compound is by first reacting an amino containing silane monomers with a cyclic carbonate to make a hydroxy urethane adduct. This adduct can be used as is or further reacted with an isocyanate or polyisocyanate to produce a silane polyurethane compound. Typical of such aforementioned silane containing polyurethane compounds are those having the following structural formula:

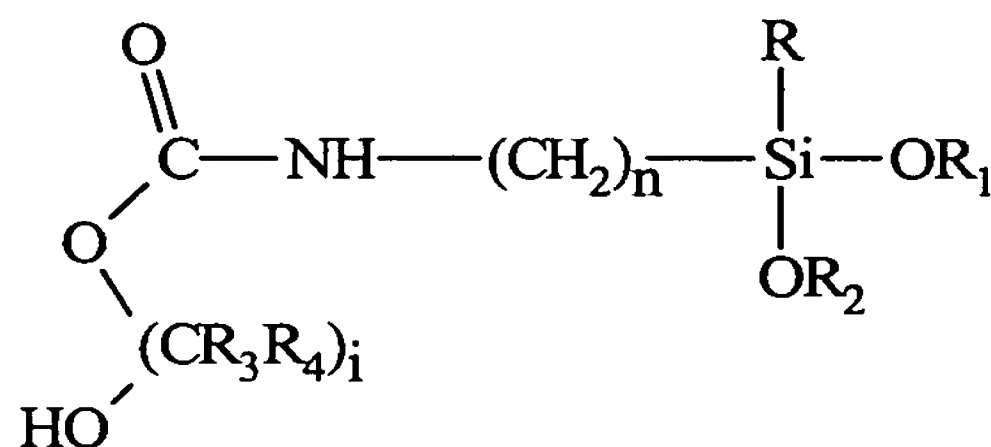
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where R is either CH<sub>3</sub>, CH<sub>3</sub> CH<sub>2</sub>, CH<sub>3</sub>O, or CH<sub>3</sub>CH<sub>2</sub>O, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>O; R<sub>1</sub> and R<sub>2</sub> are CH<sub>3</sub>, CH<sub>3</sub> CH<sub>2</sub>, or CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>; and n is 0 or a positive integer from 1 to 10, preferably from 1 to 4 (preferably, R is CH<sub>3</sub> O or CH<sub>3</sub> CH<sub>2</sub> O and n is 3); R<sub>3</sub> and R<sub>4</sub> are independently H, C<sub>1</sub>-C<sub>15</sub> alkyl, alkoxy groups, such as methoxyl, ethoxyl, phenoxy, CH<sub>2</sub>-OH, or a linked polymer structure and i is 2 or 3; and R' is a residue from an isocyanate (j=1) or a polyisocyanate (j>=1) compound.

Typical of the corresponding above-mentioned hydroxy urethane containing silane adducts are those having the following structural formula:.



where  $R, R_1, R_2, R_3, R_4, i$  and  $n$  are as described above.

The reaction for forming both the hydroxy urethane adduct and the silylated polyurethane is generally carried out at a reaction temperature in the range of from 20°C to 200°C, preferably in the range of from 40°C to 170°C, and more preferably in the range of from 50°C to 150°C. Typical reaction time is in the range of from 1 hours to 24 hours, preferably 2 to 8 hours. When the polyurethane is made, the foregoing two-step process ensures that the reactive urethane functionalities are uniformly distributed on each molecule chain of the silane oligomer. As with the other silylated urethane compounds described above, the reaction conditions are preferably chosen so that no free isocyanate groups remain in the final oligomer.

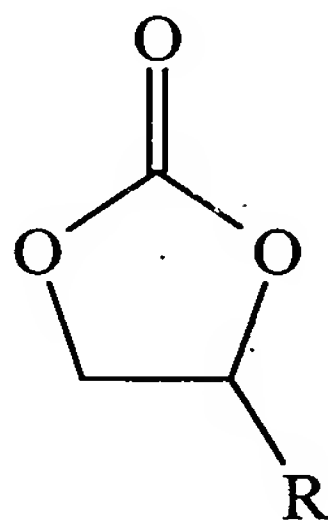
Suitable amino-group containing silane compounds that can be used to form either the adduct or polyurethane include, for example, gamma-aminopropyltrimethoxysilane, gamma-aminopropyltriethoxysilane, gamma-aminopropylmethyldimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyltrimethoxysilane, N-(beta.-aminoethyl)-gamma-aminopropyltriethoxysilane, N-(beta.-aminoethyl)-gamma.-aminopropyldimethoxysilane, and 1,3-diaminoisopropyltrimethoxysilane. However, the invention is not restricted thereto and use can be made therefore of amino group-containing silane compounds commonly employed in the art. Either



one of these amino group-containing silane compounds or a mixture of two or more thereof may be used. The aminosilane compound most preferred in the present invention is gamma-aminopropyltrimethoxysilane. Suitable cyclic carbonate compounds useful in forming the above-mentioned silane oligomer  
 5 include five membered or six member cyclic carbonates or a combination thereof. Six membered cyclic carbonates are preferred.

Some suitable cyclic carbonates that can be used to form the adduct or polyurethane include cyclic carbonates possessing one or more ring structures per molecule. The cyclic carbonate preferably contains between one to four rings,  
 10 preferably one ring. Each ring may contain 3 or 4 carbon atoms, with or without pendant side groups. The carbonate component may contain a five-member or a six-member cyclic carbonate, or a combination thereof. Six-member cyclic carbonates are preferred.

Some of the suitable five member cyclic carbonates include those having  
 15 the formula:



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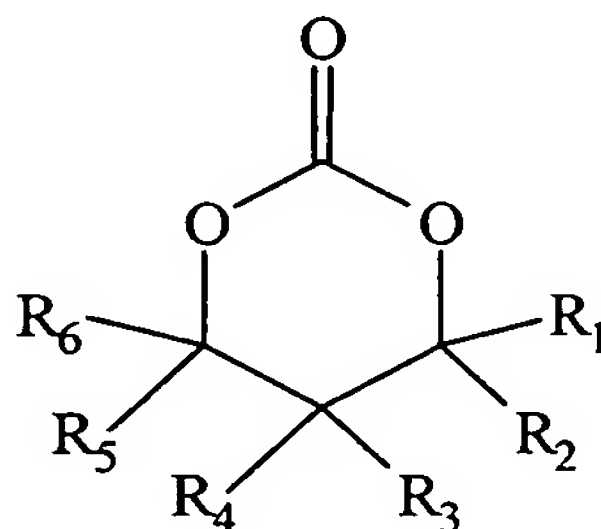
where R = H, C<sub>1</sub>-C<sub>15</sub> alkyl, alkoxy groups, such as methoxyl, ethoxyl, phenoxy, CH<sub>2</sub>-OH, or a linked polymer structure, such as from polyurethane, polyester or acrylic polymer, all of low number average molecular weight in the range of from 200 to 10,000, preferably in the range of from 300 to 5000 and more preferably in  
 25 the range of from 400 to 1000.

Five membered cyclic carbonates having 2 or more ring structures may be obtained as the reaction products of glycerin carbonate (R= CH<sub>2</sub>-OH) with aliphatic diisocyanates or polyisocyanates, such as hexamethylene diisocyanate (HMDI), isophorone diisocyanate, nonane diisocyanate, or their biuret or  
 30 isocyanurate trimers. Alternatively, a 5 membered cyclic carbonate having 2 or more cyclic carbonate ring structures may be prepared by conventional synthetic routes known within the industry which lead to polyester, polyether, or polyacrylics having such functional sites. Some of the suitable five membered cyclic carbonates include those having on average one ring structure, such as



ethylene carbonate, propylene carbonate, butylene carbonate, glycerin carbonate, butyl linseed carbonate, or a combination thereof. Ethylene, propylene, and butylene carbonates are preferred.

Some the suitable six member cyclic carbonates include those having the  
5 formula:



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where  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$ , are independently H,  $C_1$ - $C_{15}$  alkyl, or alkoxy group, such as methoxyl, ethoxyl, phenoxy, or a linked polymer structure, such as from polyurethane, polyester or acrylic polymer, all of low number average  
15 molecular weight in the range of from 200 to 10,000, preferably in the range of from 300 to 5000 and more preferably in the range of from 400 to 1000.

Six membered cyclic carbonates having on average one or more ring structure include the reaction products of dialkyl carbonates or phosgene with any 1,3 diol, such as neopentyl glycol, 1,3 propane diol, 2-methyl, 2-propyl-1,3-  
20 propanediol, or trimethylolpropane. Examples of 6 membered ring cyclic carbonates, and their synthesis are described in Examples 1, 3 and 9 in U.S. Pat. No. 4,440,937, which is incorporated herein by reference.

The present invention also includes use of six membered cyclic carbonates having on an average one or more cyclic carbonate ring structures which may be  
25 conventionally prepared by providing polyester, polyether, or polyacrylics with carbonate functionalities. Six membered cyclic carbonate functionalized polyurethanes prepared by reacting aliphatic diisocyanates or polyisocyanates with hydroxy functional carbonates, or by reacting multifunctional amines with multi ring containing cyclic carbonates are also suitable for use in the present  
30 invention.

Suitable isocyanates that can be used in the second step to form the polyurethane include any of the conventional aliphatic, cycloaliphatic, and aromatic isocyanates and polyisocyanates. Preferably, a polyisocyanate is used



having on an average 2 to 6, preferably 2 to 4 and more preferably 2 isocyanate functionalities. Examples of suitable aliphatic or cycloaliphatic polyisocyanates include aliphatic or cycloaliphatic di-, tri- or tetra-isocyanates, which may or may not be ethylenically unsaturated, such as 1,2-propylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, 1,6-hexamethylene diisocyanate, octamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, 2,4,4-trimethyl hexamethylene diisocyanate, dodecamethylene diisocyanate, omega -dipropyl ether diisocyanate, 1,3-cyclopentane diisocyanate, 1,2-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 4-methyl-1,3-diisocyanatocyclohexane, trans-vinylidene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 3,3'-dimethyl-dicyclohexylmethane 4,4'-diisocyanate, meta-tetramethylxylylene diisocyanate, polyisocyanates having isocyanurate structural units such as the isocyanurate of hexamethylene diisocyanate and isocyanurate of isophorone diisocyanate, the adduct of 2 molecules of a diisocyanate, such as hexamethylene diisocyanate, uretidiones of hexamethylene diisocyanate, uretidiones of isophorone diisocyanate or isophorone diisocyanate, and a diol such as ethylene glycol, the adduct of 3 molecules of hexamethylene diisocyanate and 1 molecule of water (available under the trademark Desmodur<sup>®</sup> N-3300 from Bayer Corporation, Pittsburgh, Pennsylvania).

Isocyanate functional adducts can also be used that are formed from an organic polyisocyanate and a polyol. One useful adduct is the reaction product of tetramethylxylidene diisocyanate and trimethylol propane and is sold under the tradename of Cythane<sup>®</sup> 3160.

Aromatic polyisocyanates can also be used, although aliphatic and cycloaliphatic polyisocyanates are generally preferred, since they have better weathering stability.

One particularly preferred silane functional compound contains the following constituents: about 15 to 25% by weight hexamethylene diisocyanate, about 30 to 60% by weight gamma-aminopropyltrimethoxysilane, and about 25 to 50% by weight propylene carbonate.

Another preferred silane functional compound, which is preferably used in conjunction with the above compound, contains the following constituents: about 50 to 70% by weight gamma-aminopropyltrimethoxysilane, and about 30 to 50% propylene carbonate.



The invention is not restricted to the silane compounds listed above and use can be made of other film-forming silane functional compounds commonly employed in the art. Also, either one of these silane compounds or a mixture of two or more thereof may be used.

5           The melamine crosslinking agents used in the composition are monomeric or polymeric melamines or a combination thereof. Partially or fully alkylated (e.g., methylated, butylated, and/or isobutylated) monomeric or polymeric melamines are preferred. The coating composition includes in the range of from about 10 to 90%, preferably in the range of from 10 to 35%, and most preferably  
10   in the range of from 10 to 30% of the melamine, the percentages being in weight percentages based on the total weight of binder solids. Lower levels of melamine may have an advantage with regard to flexibility of the primer surfacer.

          Many of the suitable melamines are supplied commercially. For example, any of the conventionally known monomeric or polymeric alkylated melamine  
15   formaldehyde resins that are partially or fully alkylated can be used. One preferred crosslinking agent is a methylated and butylated or isobutylated melamine formaldehyde resin that has a degree of polymerization of about 1-3. Generally, this melamine formaldehyde resin contains about 50% butylated groups or isobutylated groups and 50% methylated groups. Another preferred  
20   melamine formaldehyde resin is a fully butylated resin containing 100% butylated groups. Such crosslinking agents typically have a weight average molecular weight of about 500-1,500. Examples of commercially available resins are Cymel<sup>®</sup> 1168 (degree of polymerization 1.6, 50% methyl and 50% iso-butyl), Cymel<sup>®</sup> 1161 (degree of polymerization 1.4, 75% methyl and 25% iso-butyl),  
25   Cymel<sup>®</sup> 1156 (degree of polymerization 2.9, 100% butyl), and Cymel<sup>®</sup> 1158 (degree of polymerization 2.7, butyl and high imino), all of which are supplied by Cytec Industries, Inc., West Patterson, New Jersey. A preferred melamine, for a good balance of properties, is a fully butylated resin such as Cymel<sup>®</sup> 1156. Other possible crosslinking agents are urea formaldehyde, benzoquanamine formaldehyde  
30   and blocked polyisocyanates.

          Optionally, the present coating composition may further include, particularly in conjunction with optional polyol polymer or other hydroxy functional polymer, an additional crosslinking agent, for example, a blocked polyisocyanate crosslinking agent. For a one-pack system, any blocked organic  
35   polyisocyanate isocyanate can be used as the additional crosslinking agent without particular limitation, so long as the isocyanate compound has at least two isocyanate groups in the one molecule. The preferable polyisocyanate compounds



are isocyanate compounds having 2 to 3 isocyanate groups per molecule which have been blocked or capped with a blocking agent to prevent premature crosslinking in the one-pack composition. Typical examples of polyfunctional organic isocyanate compounds are any of those mentioned above used for making a urethane containing silane component, including, for instance, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, 2,4-toluene diisocyanate, diphenylmethane-4,4'-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, tetramethylxylidene diisocyanate, and the like. Trimers of diisocyanates also can be used such as the trimer of hexamethylene diisocyanate (isocyanurate) which is sold under the tradename Desmodur® N-3390, the trimer of isophorone diisocyanate (isocyanurate) which is sold under the tradename Desmodur® Z-4470 and the like. Polyisocyanate functional adducts can also be used that are formed from any of the forgoing organic polyisocyanate and a polyol. Polyols such as trimethylol alkanes like trimethylol propane or ethane can be used. One useful adduct is the reaction product of tetramethylxylidene diisocyanate and trimethylol propane and is sold under the tradename of Cythane® 3160. Since the present coating is being used to form exterior coatings, as indicated above, the use of an aliphatic or cycloaliphatic isocyanate is preferable to the use of an aromatic isocyanate, from the viewpoint of weatherability and yellowing resistance. Examples of suitable blocking agents for the polyisocyanates include lower aliphatic alcohols such as methanol, oximes such as methyl ethyl ketoxime and lactams such as caprolactam. When used, the polyisocyanate curing agent is typically present, when added to the other components which form the coating composition, in an amount ranging from about 5 to 40% by weight, preferably from about 10 to 20 % by weight, based on the total weight of binder solids in the present composition.

Optionally, but preferably, the present coating composition includes a silane coupling agent having a reactive silane group in its molecule and is different from component (a) mentioned previously. The silane coupling agent used herein is provided to wet the substrate, promote adhesion, and slow down the cure rate of the coating to enable trapped gases in the porous substrate to release before the crosslink network is finalized. The coating composition includes in the range of from 0 to 15%, preferably in the range of from 0 to 5%, and most preferably in the range of from 1 to 4% of the silane coupling agent, the percentages being in weight percentages based on the total weight of binder solids.



It is also generally preferred that the silane coupling agent used herein have in its molecule other reactive group(s) so that it might undergo some interactions with other components of the one-pack type coating composition and the substrate. It is also preferable that this compound have a relatively low weight average molecular weight of 1,000 or less so that it might exert some favorable effects on the adhesion at the substrate coating interface. As such a compound, use can be made of those which are commonly employed as silane coupling agents.

Particular examples of the silane coupling agents include amino group-containing silane compounds; epoxy group-containing silane compounds; mercapto group-containing silanes; vinyl-type unsaturated group-containing silanes; chlorine atom-containing silanes; isocyanate group-containing silanes; and hydrosilanes, though the invention is not restricted thereto.

Among these compounds, an amino group-containing silane compound is preferable from the viewpoint of imparting the above characteristics. The amino group-containing silane compound may be an arbitrary one so long as it carries amino group and reactive silane group in its molecule. Particular examples thereof include gamma-aminopropyltrimethoxysilane, gamma-aminopropyltriethoxysilane, gamma-aminopropylmethyldimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyltrimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyltriethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyldimethoxysilane, 1,3-diaminoisopropyltrimethoxysilane, N-(n-butyl)-3-aminopropyltrimethoxysilane (Dynasylan<sup>®</sup> 1189 from Degussa) and 3-ethylamino-2-methylpropyltrimethoxysilane (Silquest<sup>®</sup> A-Link 15 Silane from Crompton Corp., Greenwich, Connecticut). However, the invention is not restricted thereto and use can be made therefor of amino group-containing silane compounds commonly employed in the art. Any one of these amino group-containing silane compounds or a mixture of two or more thereof may be used.

Among the amino group-containing silane compounds as cited above, it is particularly preferable from the viewpoint of availability to use one having one secondary amino group. However, the invention is not restricted thereto.

The silane coupling agent most preferred in the present invention is a bis (3-trimethoxysilyl propyl) amine (Silquest<sup>®</sup> A-1170 from Crompton Corp.) in particular.

Optionally, the present coating composition may further include, particularly in conjunction with the melamine component, a low molecular weight



film-forming polyol compound, oligomer or polymer. It is generally preferable that at least some portion of this compound have a relatively low weight average molecular weight of 3,500 or less so that it might exert some favorable effects on wetting of the substrate. The coating composition includes in the range of from 0 to 70%, preferably in the range of from 20 to 60%, and most preferably in the range of from 30 to 55% of the polyol, the percentages being in weight percentages based on the total weight of binder solids.

Suitable polyols include acrylics, polyesters, acrylourethanes, polyester urethanes, polyurethane polyesters, polyurethanes, polyester urethane silanes, polyethers, or other polyol compounds (such as glycols), or combinations thereof. Graft polymers of different hydroxy containing resins are also suitable.

Such a polyol suitably has a hydroxyl number of about 10-200, preferably 60-140.

A suitable polyol is a polyester or polyester urethane copolymer thereof having a hydroxy number of about 10 to 200 and a weight average molecular weight of about 1,000-3,000. Preferably the T<sub>g</sub> (glass transition temperature) is below 20°C, preferably below 0°C. Such copolymers are well known to those skilled in the art and the particular monomer make-up can be selected to achieve the desired properties for a particular application, for example, depending on whether increased flexibility or increased toughness is desired.

Examples of polyesters which may be employed in this invention are suitably prepared from linear or branched chain diols, including ether glycols, or mixtures thereof or mixtures of diols and triols, containing up to and including 8 carbon atoms, in combination with a dicarboxylic acid, or anhydride thereof, or a mixture of dicarboxylic acids or anhydrides, which acids or anhydrides contain up to and including 12 carbon atoms, wherein at least 75% by weight, based on the weight of dicarboxylic acid, is an aliphatic dicarboxylic acid.

Representative saturated and unsaturated polyols that may be reacted to form a polyester include alkylene glycols such as neopentyl glycol, ethylene glycol, propylene glycol, butane diol, pentane diol, 1,6-hexane diol, 2,2-dimethyl-1,3-dioxolane-4-methanol, 4-cyclohexane dimethanol, 2,2-dimethyl 1,3-propanediol, 2,2-bis(hydroxymethyl)propionic acid, and 3-mercapto-1,2-propane diol. Neopentyl glycol is preferred to form a flexible polyester or polyurethane that is soluble in conventional solvents.

Polyhydric alcohols, having at least three hydroxyl groups, may also be included to introduce branching in the polyester. Typical polyhydric alcohols are



trimethylol propane, trimethylol ethane, pentaerythritol, glycerin and the like. Trimethylol propane is preferred, in forming a branched polyester.

The carboxylic acids include the saturated and unsaturated polycarboxylic acids and the derivatives thereof. Aliphatic dicarboxylic acids that can be used to form the polyester are as follows: adipic acid, sebacic acid, succinic acid, azelaic acid, dodecanedioic acid and the like. Preferred dicarboxylic acids are a combination of dodecandioic acid and azelaic acid. Aromatic polycarboxylic acids include phthalic acid, isophthalic acid, terephthalic acid, and the like. Cycloaliphatic polycarboxylic acids can also be used such as tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexanedicarboxylic acid and 4-methylhexahydrophthalic acid. Anhydrides may also be used, for example, maleic anhydride, phthalic anhydride, trimellitic anhydride, and the like.

Examples of polyester urethanes that can be used are the reaction product of a hydroxyl terminated polyester, as described above, and a polyisocyanate, preferably, an aliphatic or cycloaliphatic diisocyanate and any of the polyisocyanates listed above for use in the silane component may also be used in the polyester urethane.

The polyester may be prepared by conventional techniques in which the component polyols and carboxylic acids and solvent are esterified at about 110°-250°C for about 1-10 hours to form a polyester. To form the polyester urethane, a polyisocyanate may then be added and reacted at about 100°-200°C. for about 15 minutes to 2 hours.

In preparing the polyester, an esterification catalyst is typically used. Conventional catalysts include benzyl trimethyl ammonium hydroxide, tetramethyl ammonium chloride, organic tin compounds, such as dibutyl tin diaurate, dibutyl tin oxide stannous octoate and the like, and titanium complexes. About 0.1-4% by weight, based on the total weight of the polyester, of the catalyst is typically used. The aforementioned catalysts may also be used to form the polyester urethane.

The stoichiometry of the polyester preparation is controlled by the final hydroxyl number and by the need to obtain a product of low acid number; an acid number below 10 is preferable. The acid number is defined as the number of milligrams of potassium hydroxide needed to neutralize a 1 gram sample of the polyester. Additional information on the preparation of polyester urethanes is disclosed in U.S. Pat. No. 4,810,759.

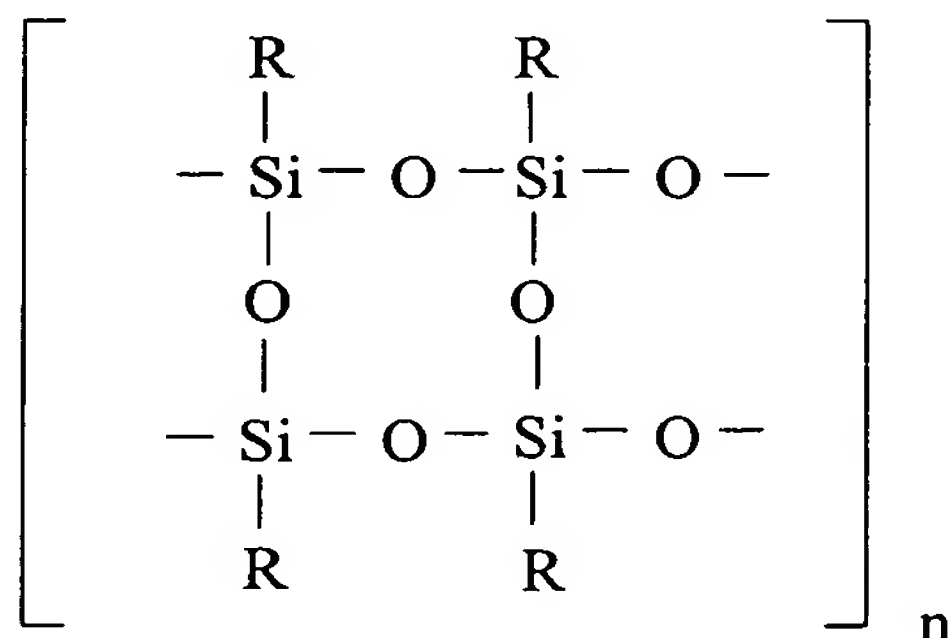


Chain extenders are also preferably used in the polyester or polyester urethane polyol component to increase flexibility of the coating film and enhance film flow and coalescence. Typically useful chain extenders are polyols such as polycaprolactone diols, such as Tone 200<sup>®</sup> series available from Union Carbide/Dow Corporation. Caprolactones such epsilon-caprolactone may also be reacted with the polyols cited above for chain extension, as is well known in the art.

The invention is not restricted to the polyesters and polyester urethanes listed above and use can be made of other film-forming polyol compounds commonly employed in the art. Also, either one of these polyols or a mixture of two or more thereof may be used.

Another optional binder component in the coating composition of the present invention is one or more reactive dispersed particles (oligomer or polymer) with at least one functional group (such as silane or hydroxy group) that is capable of reacting with the silane and/or melamine component. The dispersed particle is provided to prevent cracking of the film which crosslinked silane coatings are otherwise prone.

Examples of dispersed particles include oligosilsesquioxanes, also referred to herein as silsesquioxanes. Such silsesquioxanes may suitably be present in the amount of 0 to 10% by weight, based on the weight of the binder, preferably about 1 to 10%, to improve the crack resistance of the resulting coating. Silsesquioxane compounds are oligomers that may be visualized as composed of tetracyclosiloxane rings, for example as follows:



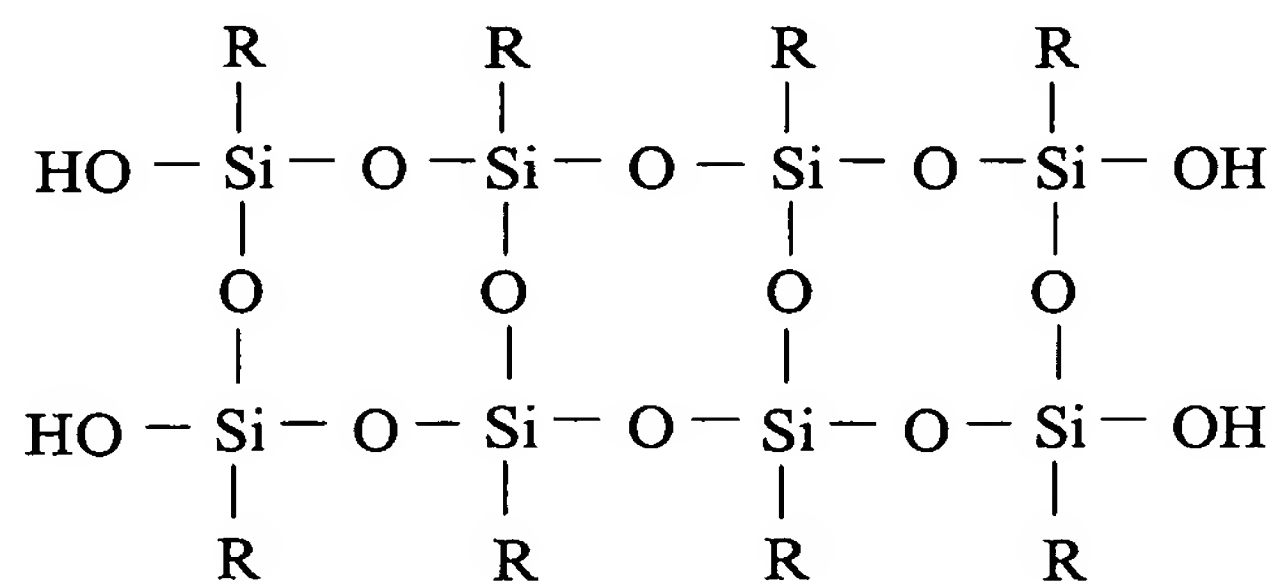
25

The number of repeating units is suitably 2 or more, preferably 2 to 12. Exemplary compounds, commercially available from Petrarch Systems, Inc.



(Bristol, Pa.) include polymethylsilsesquioxane, polyphenylpropylsilsesquioxane, polyphenylsilsesquioxane, and polyphenylvinylsilsesquioxane.

Such silsesquioxanes have a plurality of consecutive  $\text{SiO}_3\text{R}$ - groups, forming  $\text{SiO}$  cages or "T" structures or ladders. The various rough geometries depend on the  $n$  in the above formula, which may vary from 2 to 12 or greater. These silsesquioxane compounds should have at least 1 hydroxy group, preferably at least 4. However, the greater the number of hydroxy groups, the greater the amount of crosslinking. Lower functionality is generally desired. A preferred polysilsesquioxane may be depicted as having the following structural formula:



10

In the above formula, R is a substituted or unsubstituted alkyl, alkoxy or phenyl or combination thereof. Substituents include hydroxy, halo groups such as fluoro, and haloalkyl groups such as trifluoromethyl. As one example, in the above formula, R may consist of about 70 mole percent of phenyl and 30 mole percent propyl. Such a compound is commercially available as Z-6018 from Dow Corning. This compound has a weight average molecular weight of 1,600, 4 SiOH groups, and an OH equivalent weight of 330-360.

Dispersed polymer particles containing silane or hydroxy functionality, for crosslinking purposes, can also be used. These polymers are commonly referred to as NAD (non-aqueous dispersion) polymers. Suitable dispersed polymers for use in conjunction with silane polymers are disclosed in U.S. Pat. No. 5,250,605, hereby incorporated by reference in its entirety. These dispersed polymers, like the silsesquioxanes cited above, are known to solve the problem of cracking heretofore associated with silane coatings.

A catalyst is typically added to the coating composition of the present invention to catalyze the crosslinking of the silane moieties of the silane component with itself and with other components of the composition. Typical of such catalysts are dibutyl tin dilaurate, dibutyl tin diacetate, dibutyl tin dioxide, dibutyl tin dioctoate, tin octoate, aluminum titanate, aluminum chelates,



zirconium chelate and the like. Catalysts useful for catalyzing melamine reactions include the conventional acid catalysts, such as aromatic sulfonic acids, for example dodecylbenzene sulfonic acid, para-toluenesulfonic acid and dinonylnaphthalene sulfonic acid, all of which are either unblocked or blocked  
5 with an amine, such as dimethyl oxazolidine, 2-amino-2-methyl-1-propanol, n,n-dimethylethanolamine, n,n-diisopropanolamine, or a combination thereof. Other acid catalysts that can be used are strong acids, such as phosphoric and phosphonic acids which may be unblocked or blocked with an amine. Combinations of two or more of the above catalysts can also be used. Preferably,  
10 these catalysts are used in the amount of about 0.1 to 5.0%, more preferably about 0.1 to 2% by weight of the binder.

A suitable amount of water scavenger such as trimethyl orthoacetate, triethyl orthoformate, tetrasilicate and the like (0.1-15% by weight, preferably 2 to 10% by weight of binder) may be added to the coating composition to react with  
15 water in the substrate cavities and further minimize popping defects. Water scavengers are also useful for extending shelf life of this moisture sensitive composition. Up to about 1-3% silica may be employed for rheology control. The composition may also include other conventional formulation additives such as UV stabilizers, toughening agents, and flow control agents, for example, such  
20 as Resiflow® S (polybutylacrylate), BYK® 320 and 325 (high molecular weight polyacrylates). Such additional additives will, of course, depend on the desired final properties of the coating composition.

Primer-surfacers also typically contain pigments to provide properties such as hiding, sandability, adhesion, reduced cost, and to render the composition  
25 amenable to topcoat application. Primer-surfacers are often color keyed to the color family of the colorcoat (i.e., basecoat) finish that is subsequently applied directly thereover. This is done to enable the colorcoat to achieve complete hiding at the lowest possible film build. Accordingly, in these cases, sufficient amounts of pigment(s) are also used to impart the appropriate color to the composition.

30 Typical pigments that can be added include the following: metallic oxides such as titanium dioxide, zinc oxide, iron oxides of various colors, carbon black, extender pigments such as talc, china clay, barytes, carbonates, silicates and a wide variety of organic colored pigments such as quinacridones, copper phthalocyanines, perylenes, azo pigments, indanthrone blues, carbazoles such as  
35 carbazole violet, isoindolinones, isoindolones, thioindigo reds, and benzimidazolinones, and the like. The resulting composition when used as a



primer surfacer usually has a pigment to binder weight ratio of about 1:100-150:100.

5 While conventional primer surfacer coatings in the automotive industry are generally non-conductive, the present coating composition can be rendered conductive, if desired, to facilitate subsequent electrostatic application of the topcoat paints, such as the colored basecoat, to the plastic part. Therefore, the composition of the present invention may include at least one conductive pigment in an amount sufficient to impart conductivity to the coating film upon curing. Suitable conductive pigments include carbon black, graphite and mixtures of the  
10 two.

The pigments can be introduced into the coating composition by first forming a mill base or pigment dispersion with any of the aforementioned polymers/oligomers used in the coating composition or with another compatible polymer or dispersant by conventional techniques, such as mixing/slurrying, high  
15 speed mixing, media milling, sand grinding, ball milling, attritor grinding or two/three roll milling. The pigment dispersion is then blended with the other constituents used in the coating composition.

The coating composition of the present invention, which is preferably formulated into high solids coating systems further contains at least one organic  
20 solvent typically selected from the group consisting of aliphatic or aromatic hydrocarbons such as petroleum naphtha or xylenes; ketones such as methyl amyl ketone, methyl isobutyl ketone, methyl ethyl ketone or acetone; alcohols such as methanol, isopropanol, or butanol; esters such as butyl acetate or hexyl acetate; glycol ethers such as ethylene glycol monethyl ether; glycol ether esters, such as  
25 propylene glycol monomethyl ether acetate and petroleum distillate cuts such as Aromatic 100, from Exxonmobil Chemical Co., Houston, Texas. The amount of organic solvent added depends upon the desired viscosity as well as the desired amount of VOC of the composition. If desired, the organic solvent may be added to each component of the binder.

30 The coating composition of the present invention is typically supplied as a one-pack coating composition in which all ingredients are mixed and stored together in the same container. The composition is preferably stored in a moisture-proof sealed container to prevent degradation during storage. The one-pack coating according to this invention thus obtained does not cure during the  
35 storage period. When it is taken out of the container and exposed to moisture in the atmosphere, it begins to cure from the surface. Of course, it can be formulated



as a two-pack coating as will occur to one skilled in the art, although a one-pack composition is generally preferred.

The composition of the present invention may be applied by conventional techniques such as spraying, electrostatic spraying, high rotational electrostatic  
5 bells and the like. The preferred techniques are air atomized spraying with or without electrostatic enhancement, and high speed rotational electrostatic bells, since these techniques are typically employed in a continuous paint application processes. After application, the composition is typically baked at 150-300°C, usually under gradual heating, for about 30-50 minutes to sufficiently degas the  
10 substrate and form a barrier coating about 0.1-2.0 mils thick.

Useful substrates that can be coated according to the process of the present invention include a variety of metallic and non-metallic substrates such as plastic substrates, and combinations thereof. Useful metallic substrates that can be coated according to the process of the present invention include unprimed  
15 substrates or previously painted substrates, cold rolled steel, phosphatized steel, and steel coated with conventional primers by electrodeposition. Useful plastic materials include molded fiberglass reinforced polyesters such as SMC, polyester reinforced fiberglass, reaction-injection molded urethanes, partially crystalline polyamides, and the like or mixtures thereof and their associated primers. The  
20 plastic substrates can also include any other thermoset or thermoplastic part, reinforced or not reinforced, as will readily occur to one skilled in the art. Preferably, the plastic substrates are sealed prior to application, although the primer surfacer of this invention can also be used as a sealer or sealerless primer composition. More preferably, the substrates that are coated according to the  
25 present invention are used as components to fabricate automotive vehicles, including but not limited to automobiles, trucks, and tractors, and watercrafts including but not limited to boats, wave-runners, and jet skis. The substrates can have any shape, but are usually in the form of either automotive body components such as bodies, hoods, doors, fenders, bumpers and/or trim for automotive  
30 vehicles, or watercraft body components such as hulls, trim for boats, and the like. The substrate may also be appropriately degassed immediately prior to primer surfacer application.

When the coating composition of this invention is used as a primer surfacer in automotive applications, it is customary to first attach the sealed SMC  
35 or other sealed plastic part to the frame of the vehicle and then have the sealed plastic part travel on the vehicle through the standard electrocoat tanks where only the steel parts on the vehicle get electrocoated with electrodeposition primers.



Thereafter, the primer surfacer of this invention is applied over the entire vehicle body exterior including over the sealed plastic part to cover imperfections and provide a smooth finish and then the sealed plastic part along with the vehicle body are finished with a conventional automotive exterior monocoat,  
5 baseocat/clearcoat, or tricoat finish.

Upon curing of the coating composition of the present invention, the coating has excellent barrier properties and exhibits low paint defects during the OEM finishing operations which eliminates extensive reworking and repainting of the part.

10 While the composition of this invention is particularly useful as a primer surfacer, it can also be used as a pigmented monocoat or basecoat finish over a variety plastic parts, due to its excellent adhesion to plastics, durability, and resistance to yellowing on baking and on exposure to outdoor weathering.

The invention will now be illustrated in the following Examples. All parts  
15 and percentages are on a weight basis unless otherwise indicated.

### **EXAMPLES**

The following SMC primer surfacer compositions according to the present invention were prepared and tested for barrier properties over previously sealed  
20 SMC subjected to stress forces (post stress).

#### **Example 1**

##### **Preparation of Primer Surfacer Composition 1**

A primer surfacer sealer composition according to the present invention was prepared by blending together the following ingredients in the amounts given  
25 using the following procedure:

25.0 g reactive silane functional polyurethane component 1 (described in Resin Example 1,A. below), 70.0 g of a branched polyester (described in Resin Example 1,D. below), 25.0 g Cymel<sup>®</sup>1156 (alkylated melamime formaldehyde crosslinking) from Cytec Industries, 40.0 g of an blocked aliphatic polyisocyanate  
30 (Desmodur<sup>®</sup> BL3175A) from Bayer Polymers, 2.0 g of a flow aid (Disparlon<sup>®</sup> LC-955) from King Industries, 0.1 g Fascat<sup>®</sup> 4202 (Atofina Chemicals) (dibutyl tin-dilaurate catalyst), 12.0 g of a 65% solution of a polymeric dodecylbenzene sulfonic acid ester catalyst (Nacure<sup>®</sup> 5414) from King Industries, 2.5 g Silquest<sup>®</sup> A-1170 (silane coupling agent) from OSi Specialties, 5.0 g of a 75% solution of  
35 Z-6018 intermediate (Dow Corning) (low molecular weight hydroxy functional



silicone (silsesquioxane) particulate), and 12.5 g reactive silane functional component 2 (described in Resin Example 1,C. below) were loaded into a container and mixed well. Then to this mixture, the following dispersions were added: 74.2 g of a 204 pigment-to-binder ratio (P/B) barium sulfate (Huberite<sup>®</sup> #1 from J.M. Huber Corp.) dispersion in polyester, 38.2 g of a 106 P/B dispersion of magnesium silicate (Mistron<sup>®</sup> Monomix from Luzenac America) in melamine/polyester, 23.9 g of a 43 P/B dispersion of colloidal synthetic silica (Syloid<sup>®</sup> 378, grade 78, from W.R. Grace) in polyester, 8.8 g of a 86 P/B dispersion of carbon black (Raven<sup>®</sup> 5000 Ultra II Beads from Columbian Chemicals Company) in a blend of a polyester comb polymer described in US 6,037,414 at 55/100 polymer/pigment solids and an acrylic block copolymer described in US 4,656,226 at 45/100 polymer/pigment solids and 5% weight % of trimethyl orthoformate from Nippon Chemicals, 9.7 g of a 607 P/B dispersion of titanium dioxide (Ti-Pure<sup>®</sup> Rutile R706 01 from DuPont Company), 10.1 g of a 36 P/B dispersion of quinacridone violet (Sunfast<sup>®</sup> Violet 228-0639 from Sun Chemical) in polyester, and 8.0 g of a 500 P/B dispersion of a yellow orange iron oxide (Bayferrox<sup>®</sup> 1420 from Bayer Chemical) in acrylic dispersant and polyester. After mixing well, the mixture was reduced to spray viscosity (30 sec in a Ford #4 cup), 8-15% by weight, with Aromatic150 solvent (ExxonMobil).

20

### Example 2

#### Preparation of Primer Surfacer Composition 2

Another primer surfacer sealer composition according to the present invention was prepared by blending together the following ingredients in the amounts given using the following procedure:

29.4 g reactive silane functional polyurethane component 3 (described in Resin Example 1,E. below), 70.0 g of a branched polyester (described in Resin Example 1,D. below), 25.0 g Cymel<sup>®</sup> 1156 (alkylated melamime formaldehyde crosslinking) from Cytec Industries, 40.0 g of an blocked aliphatic polyisocyanate (Desmodur<sup>®</sup> BL3175A) from Bayer Polymers, 2.0 g of a flow aid (Disparlon<sup>®</sup> LC-955) from King Industries, 0.1 g Fascat<sup>®</sup> 4202 (Atofina Chemicals) (dibutyl tin-dilaurate catalyst), 12.0 g of a 65% solution of a polymeric dodecylbenzene sulfonic acid ester catalyst (Nacure<sup>®</sup> 5414) from King Industries, 2.5 g Silquest<sup>®</sup> A-1170 (silane coupling agent) from OSi Specialties, 5.0 g of a 75% solution of Z-6018 intermediate (Dow Corning) (low molecular weight hydroxy functional silicone (silsesquioxane) particulate), and 12.5 g reactive silane functional component 2 (described in Resin Example 1,C. below), were loaded into a container and mixed well. Then to this mixture, the following dispersions were



added: 74.2 g of a 204 pigment-to-binder ratio (P/B) barium sulfate (Huberite<sup>®</sup> #1 from J.M. Huber Corp.) dispersion in polyester, 38.2 g of a 106 P/B dispersion of magnesium silicate (Mistron<sup>®</sup> Monomix from Luzenac America) in melamine/polyester, 3.9 g of a 43 P/B dispersion of colloidal synthetic silica (Syloid<sup>®</sup> 378, grade 78, from W.R. Grace) in polyester, 8.8 g of a 86 P/B dispersion of carbon black (Raven<sup>®</sup> 5000 Ultra II Beads from Columbian Chemicals Company) in a blend of a polyester comb polymer described in U.S. Pat. No. 6,037,414 at 55/100 polymer/pigment solids and an acrylic block copolymer described in U.S. Pat. No. 4,656,226 at 45/100 polymer/pigment solids and 5% weight of trimethyl orthoformate from Nippon Chemicals, 9.7 g of a 607 P/B dispersion of titanium dioxide (Ti-Pure<sup>®</sup> Rutile R706 01 from DuPont), 10.1 g of a 36 P/B dispersion of quinacridone violet (Sunfast<sup>®</sup> Violet 228-0639 from Sun Chemical) in polyester, and 8.0 g of a 500 P/B dispersion of a yellow orange iron oxide (Bayferrox<sup>®</sup> 1420 from Bayer Chemical) in acrylic dispersant and polyester. After mixing well, the mixture was reduced to spray viscosity (30 sec in a Ford #4 cup), 8-15% by weight, with Aromatic150 solvent (ExxonMobil).

The following premixes were used to prepare the primer surfacer sealer compositions of Examples 1 and 2:

#### Resin Example 1,A

##### Preparation of Silane Functional Polyurethane Component 1

To a reactor fitted with heating mantle, stirrer and under nitrogen blanket, 2761.22 parts of g-aminopropyltrimethoxy silane (Silquest<sup>®</sup> A1110 from Greenwich, Connecticut ), 100 parts of ethyleneglycol monobutylether acetate (Butyl cellusolve acetate from Dow Chemical, Midland, MI) and 1650.957 parts of propylene carbonate (from Huntsman Corporation, Austin TX) were added and heated under agitation to 80C. The mixture was held at 80C for 4 hours. Then a mixture of 440 parts ethyleneglycol monobutylether acetate, three drops parts of dibutyltin dilaurate (Fascat<sup>®</sup> 4202 catalyst from Atofina Chemicals, Philadelphia, Pennsylvania) and 1260 parts of hexamethylene diisocyanate (Desmodur<sup>®</sup> H, from Bayer Corporation, Pittsburgh, Pennsylvania) was added at a rate to keep the exotherm below 100°C (approximately 150 minutes). Then 100 parts ethyleneglycol monobutylether acetate was added and the reaction mixture held at 90-110°C for three hours. Then 250 parts of isopropyl alcohol was added as a shot and the reaction held for 60 minutes at 90°C at which point the isocyanate had been completely consumed as determined by the absence of the isocyanate absorbance at 2220 cm<sup>-1</sup> in the infrared spectrum. Then 1398.125 parts of cyclohexydimethylene/caprolactone adduct additive (described in Resin Example



1,B. below) and 390 parts of ethyleneglycol monobutylether acetate were added and the resin cooled. The resulting silane functional polyurethane polymer/polyester blend had a solids content of 80% by weight.

### **Resin Example 1,B**

#### **5      Preparation of CHDM/Caprolactone Adduct Additive for Silated Urethane 1,A**

To a reactor fitted with heating mantle, stirrer and under nitrogen blanket, 628.25 parts of 2-Oxepanone (Tone<sup>®</sup> Monomer EC,HP from Dow Chemical, Midland MI) were charged. Then 264.55 parts of molten 1,4 cyclohexanedimethanol (CHDM-D from Eastman Chemical) were added. A shot  
10 0.122 parts of dibutyltin dilaurate (Fascat 4202 catalyst from Atofina Chemicals) were added and 1.078 parts of xylene were then added and the reaction mixture heated to 125°C. The temperature was allowed to exotherm to 140°C and was then held at 140°C for four hours. The reaction mixture was then cooled to yield a hydroxyl containing polyester resin at 98% solids.

### **15      Resin Example 1,C**

#### **Preparation of Silane Functional Component 2**

To a reactor fitted with heating mantle, stirrer, condenser, and under nitrogen blanket, 491.32 parts of g-aminopropyltrimethoxy silane (Silquest<sup>®</sup> A1110 from Crompton Corp.) and 288.08 parts of propylene carbonate (from  
20 Huntsman Corporation, Austin TX) were added and heated under agitation to 120°C. The mixture was held at 120°C for 4 hours. Then 44.6 parts of n-butanol were added and the reaction mixture cooled. The resulting hydroxy functional silane oligomer had a solids content of 94% by weight

### **Resin Example 1,D**

#### **25      Preparation of Branched Polyester Polyol Resin**

To a reactor with a heating mantle, stirrer, condenser and decanter, the following components were added in order with mixing at 50-80C: 200.18 parts of a 90% aqueous solution of neopentyl glycol, 53.96 parts of 1,6-hexanediol (BASF Corporation), 115.290 parts of trimethylolpropane, 94.580 parts of  
30 isophthalic acid, 294.63 parts of azelaic acid (Emerox<sup>®</sup> 1144 azelaic acid from Cognis Corp), 63.64 parts of phthalic anhydride. The reaction mixture was heated to 240-250°C and water was removed by azeotropic distillation with xylene until the acid number was less than 5 mg KOH/g resin. Then 61.12 parts of xylene were added and the resin cooled. Thereafter 14.57 parts of toluene and 11.7 parts



of xylene were added with mixing. Finally 76.98 parts of methyl ethyl ketone were added. The reactor product was a polyester resin of 80% solids.

### **Resin Example 1,E**

#### **Preparation of Silane Functional Component 3**

5 To a reactor fitted with heating mantle, stirrer, condenser, thermocouple, and under a nitrogen blanket, 375 parts of an aromatic hydrocarbon (Aromatic 100 from ExxonMobile Chemical), 125 parts of n-butanol (N-Butanol from Dow Chemical, Midland MI) and 500 parts of vinyl trimethoxy silane (Silquest<sup>®</sup> A-171, GE Silicones) were added and heated to reflux (approximately 125°C) under  
10 agitation. To this a monomer mixture consisting of 925 parts of isobornyl acrylate (Sipomer<sup>®</sup> IBOA-HP STD from Rhodia), 75 parts of isobutyl methacrylate (from Lucite International), 500 parts of hydroxypropyl acrylate (Bisomer<sup>®</sup> HPA from Cognis Performance Chemicals UK, LTD), and 500 parts of n-butyl acrylate (Dow Chemical, Midland, Michigan) were fed over a period of 240 minutes.  
15 Simultaneously, an initiator mixture consisting of 160 parts of n-butanol, 160 parts of Aromatic 100, and 50 parts of tert-butylperoxy ethylhexanoate (Luperox<sup>®</sup> 26 from Atofina, ) were added over 360 minutes. Reflux was maintained during the feeds. After completion of the initiator mixture feed, the reaction mixture was held at reflux for an additional 30 minutes. Then 104 parts of Aromatic 100 were  
20 added and the mixture cooled. The resulting silane functional polyol had a solids content of 72% by weight and a V Gardner-Holt viscosity.

### **Example 3**

#### **Evaluation of Primer Surfacer Properties**

Two conductive primer-sealers, a commercial 2K sealer (Redspot 2560E)  
25 and an experimental 1K sealer (Example 1 of copending U.S. Patent Application No. 10/623,710) were spray-applied to 1.0 mil over two separate commercial compression-molded SMC panels (2" wide by 18" long strips with a thickness of 0.1") which had been appropriately cleaned of dirt prior to sealer application. The panels were flashed for 10 min at room temperature and then baked at 200°F for  
30 17 min, followed by 240°F for 17 min, followed by 300°F for 17 min to simulate a real-world ramp bake profile. This was followed, after undergoing a stress and humidification procedure described below, by a 30 min 400°F bake to simulate the e-coat bake the SMC part would see in the OEM assembly plant.

After a second humidification as described below, panels were allowed to  
35 stand for 16 hours under ambient conditions, each of the primer surfacers from Examples 1 and 2 and a commercial OEM gray primer-surfacer (from DuPont



Company) with the same pigmentation were spray-applied to 1.0 mil thickness separately over each sealer described above and baked at 300°F for 30 min. Panels were then topcoated wet-on-wet with commercial OEM high solids black basecoat and clearcoat (from DuPont Company) (0.7 and 1.8 mils, respectively) and baked 30 min at 285°F.

Coatings were analyzed for resistance to pop defects under a post-stress condition, i.e., simulation of damage to SMC that would occur at the molder, in shipping, and at the OEM assembly plant after SMC primer application. To simulate post-stress conditions, each primed SMC panel was exposed to stress by flexing before the e-coat bake simulation. Each panel was placed so that the back of the panel was in contact with an 8.25" cylindrical mandrel. Starting by holding one end of the strip to the mandrel in a tangent position, the other end was pulled to the center of the mandrel until the panel conformed to the circumference, held for five seconds, then released, allowing the specimen to return to a relaxed state.

The test panels were also subjected to humidification cycles to simulate part shipping and assembly in humid environments. Each panel received a sixteen hour humidity exposure (100% RH, 100°F) before sealer application. After the sealer was applied and baked, and the panel stressed, each panel received a second sixteen hour humidity exposure (80% RH, 77°F).

Three judges examined the sealed and topcoated SMC panels and tallied the pop counts at each stage. Each judge had considerable experience with, and knowledge of, paint defects that occur on plastic components.

The average number of pops observed in the topcoat layer under post-stress conditions for each system described above is shown in Table 1. This post-stress pop count data is also depicted in FIG. 1. No popping was observed after sealer application and bake as panels had not been subjected to any stress damage. However, subjecting these panels to the stress/humidity condition described above produces a significant amount of popping after applying primer-surfacer and topcoat. The data shows the primer surfacers of this invention to outperform the commercial SMC primer-surfacer.



Table 1 – Topcoat Pop Counts

	Commercial 2K Sealer <sup>1</sup>	Experimental 1K Sealer <sup>2</sup>
Control Primer Surfacer <sup>3</sup>	350	40
Primer Surfacer Example 1	90	15
Primer Surfacer Example 2	75	10

Table Footnotes

1. 1K SMC Sealer Prepared according to the procedure described in Example 1 of U.S. Patent Application No. 10/623,710.
- 5 2. DuPont 708-DT382 (medium graphite) commercial SMC primer surfacer.
3. Redspot 2560E 2K isocyanate commercial SMC sealer.

On the whole, it has been found that the presence of silane compound(s) in the primer-surfacer composition according to the present invention substantially improves the appearance of the coating with substantially better post stress pop resistance.

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